

# EMPA/BUWAL studies on NO<sub>2</sub> emissions

NO<sub>2</sub> emissions by city buses

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*IDRAC 5 October 2004*

# BUWAL studies on NO<sub>2</sub> (1)

- These studies are not yet published, but released for the use within CARB
- These studies are complete appreciations of the exhaust control technologies
- CRTs show excellent performances in controlling PM mass and number
- But there is a serious concern about NO<sub>2</sub> especially at low load (city driving pattern)

# BUWAL studies on NO<sub>2</sub> (2)

- The main purpose of the first study was to check emissions from a Euro 2 engine equipped with a CRT for 7 months (Volvo)
- Reference emissions are those of 1990 (Euro 0) engines recently retrofitted with a CRT (NAW and Mercedes buses)
- Volvo bus was operated with 10 and 50 ppm S, NAW with 50 ppm and Mercedes with 10 ppm

# Original report available at EMPA

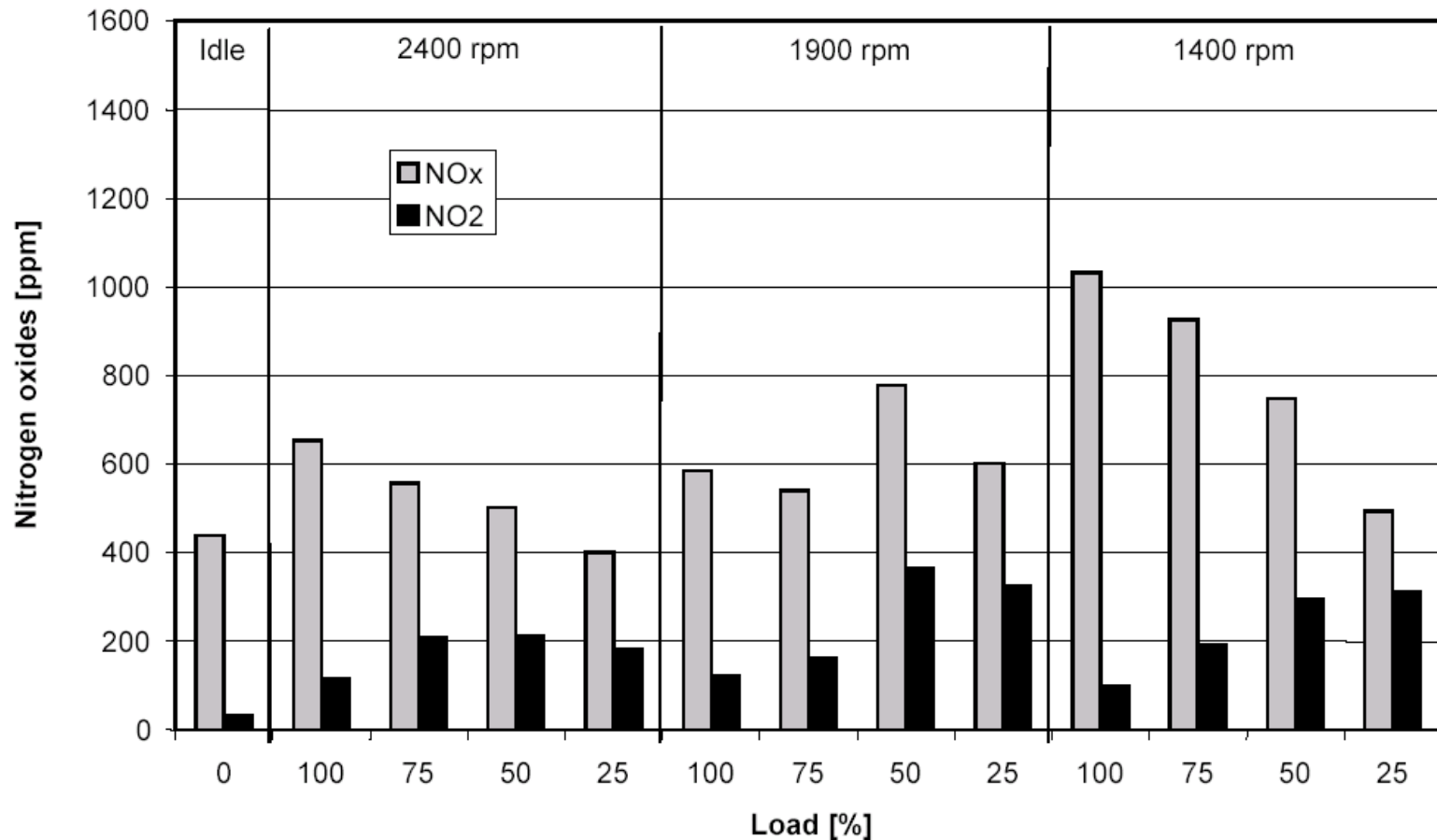
**Report of EMPA on Euro 0 and Euro 2 buses fitted with commercial CRT**

Report No. 411289 / 2  
Air Pollution / Environmental Technology Laboratory

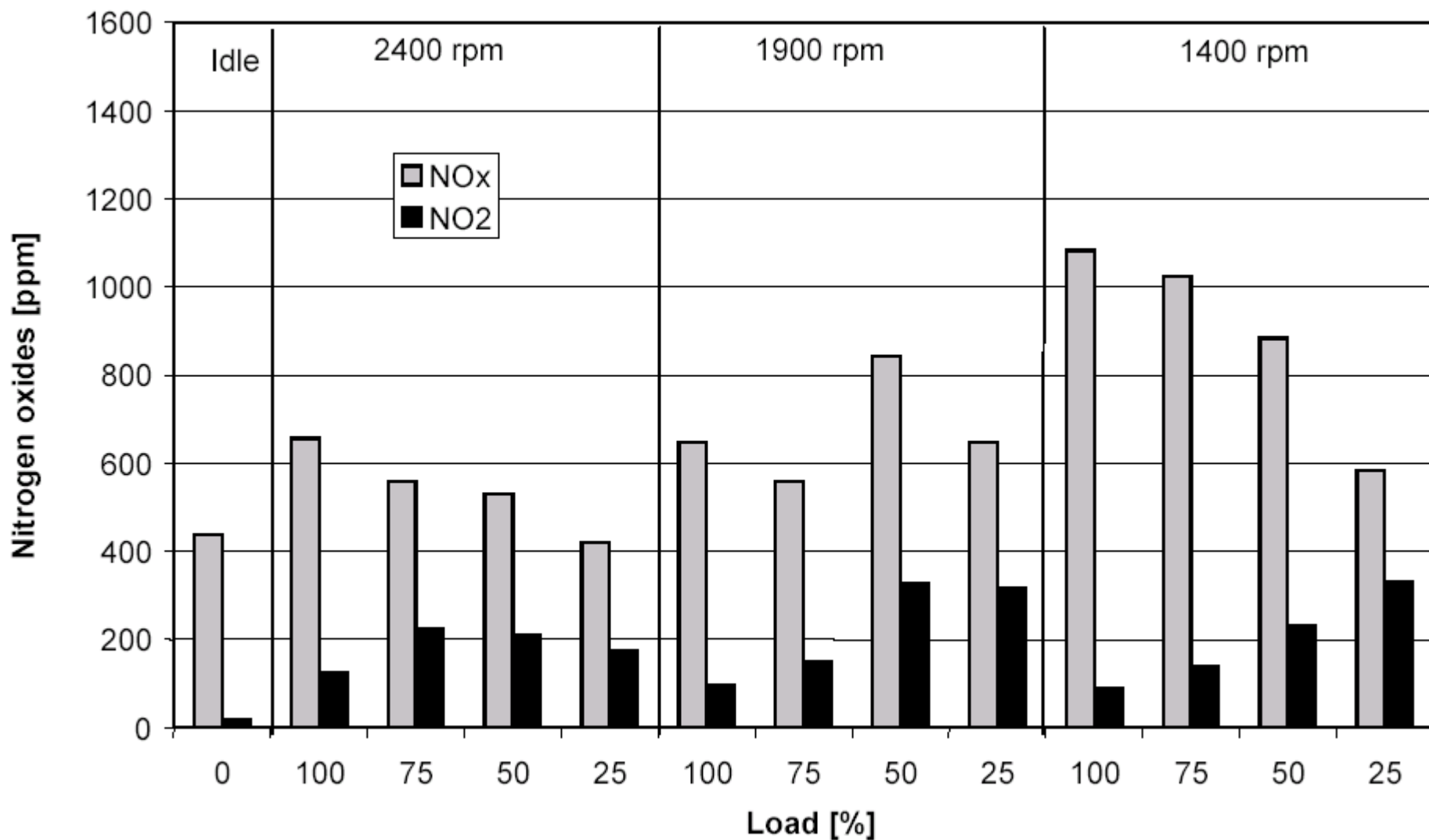


**Contact person at EMPA: Lukas Hemmenegger** [lukas.hemmenegger@empa.ch](mailto:lukas.hemmenegger@empa.ch)

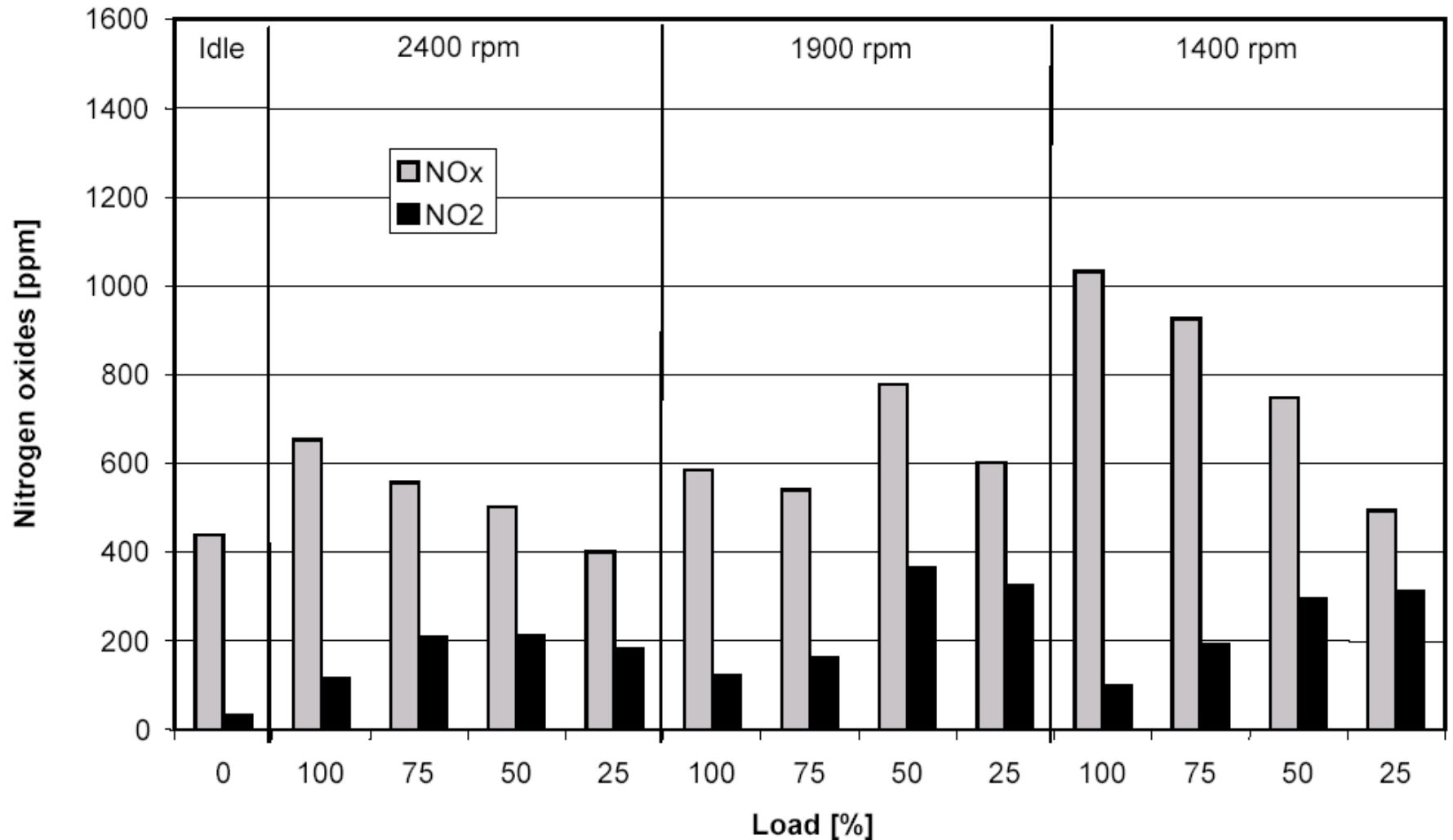
# NO<sub>x</sub> & NO<sub>2</sub> at exhaust of a Mercedes bus fitted with a CRT



*Fig. 1: Nitrogen oxide concentrations from vehicle No.1 (SG 3309, 50 ppm S)*



*Fig. 2: Nitrogen oxide concentrations from vehicle No. 2 (SG 3309, 10 ppm S)*



*Fig. 3: Nitrogen oxide concentrations from vehicle No. 3 (ZH 540689)*

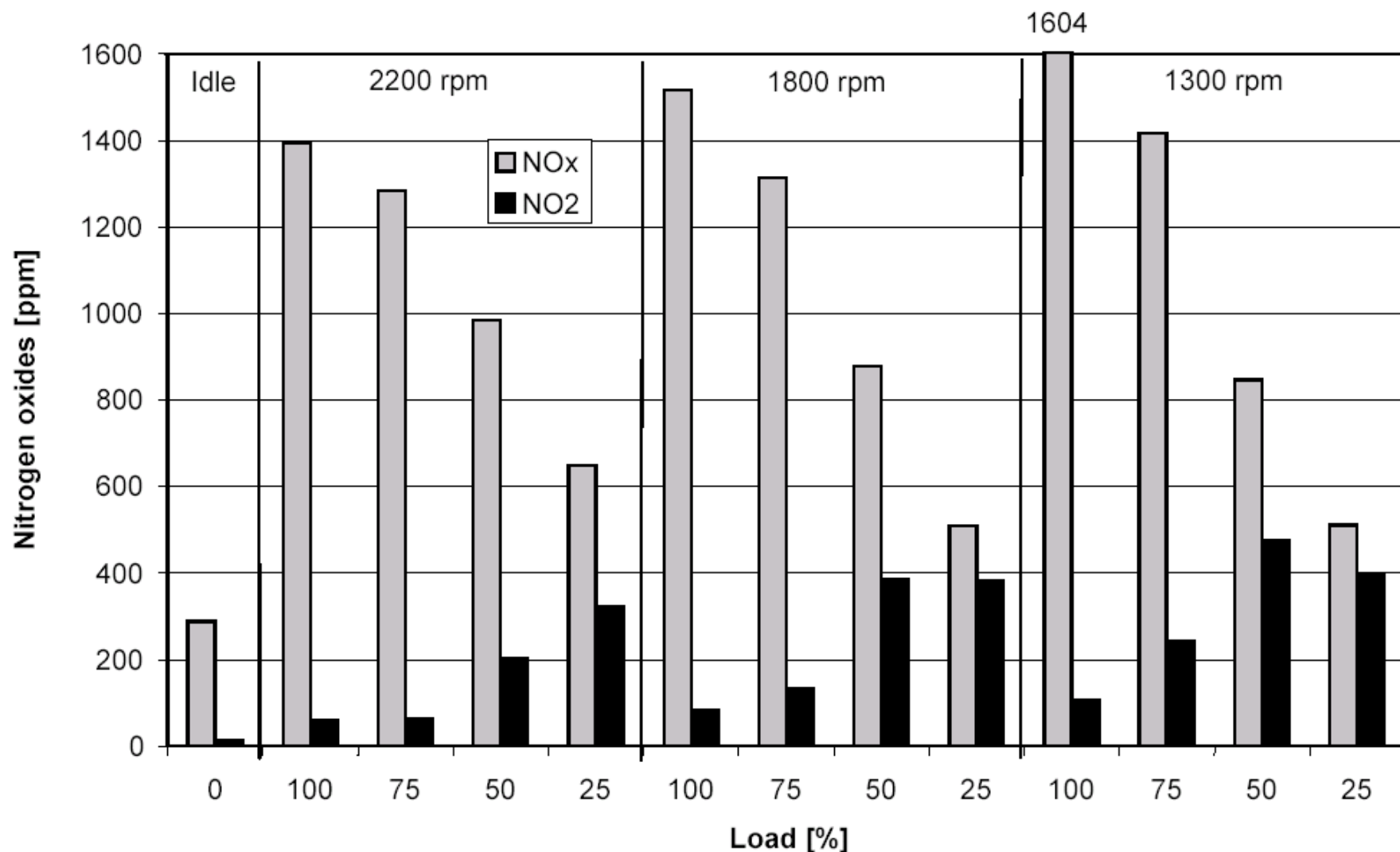
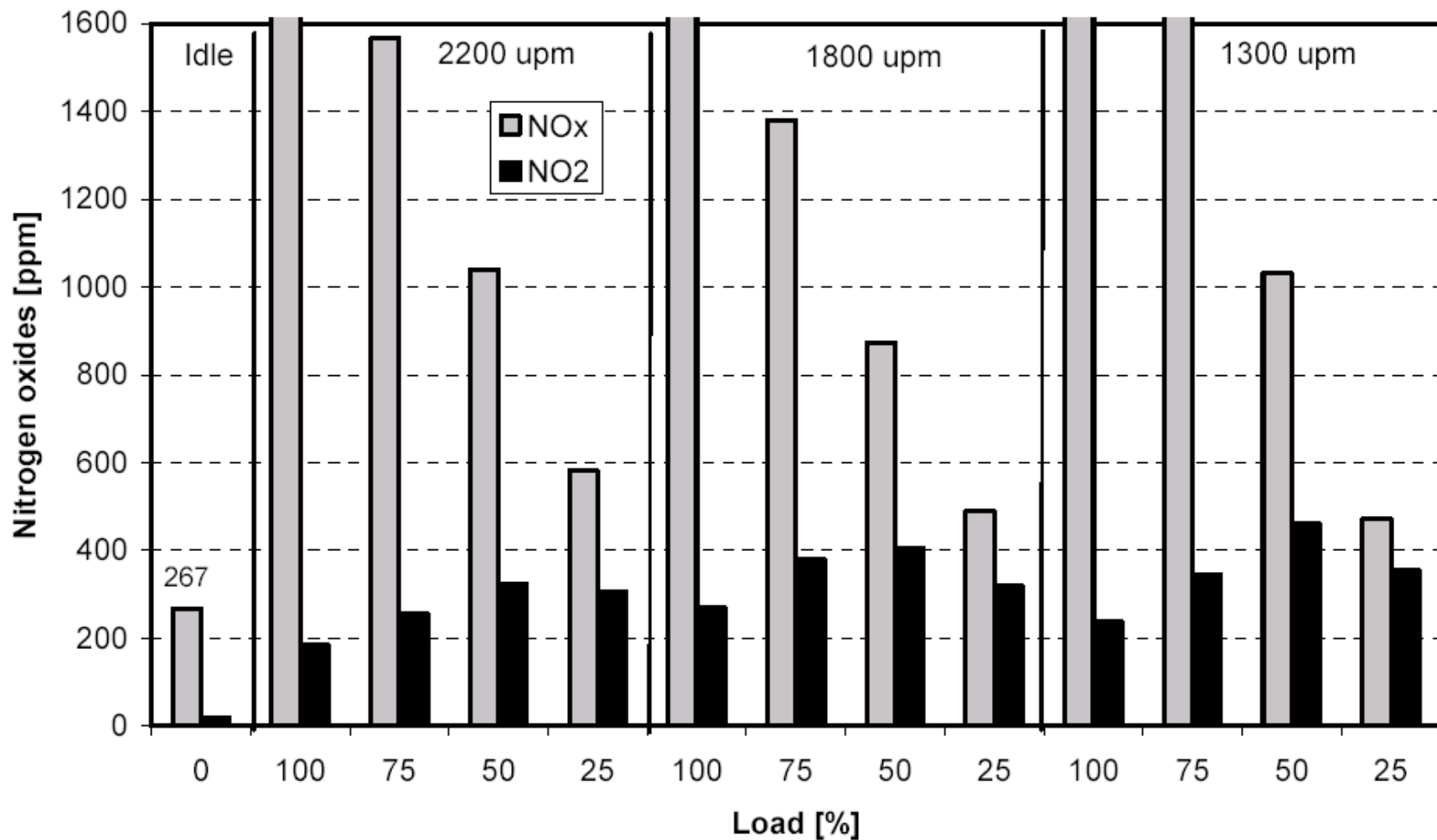
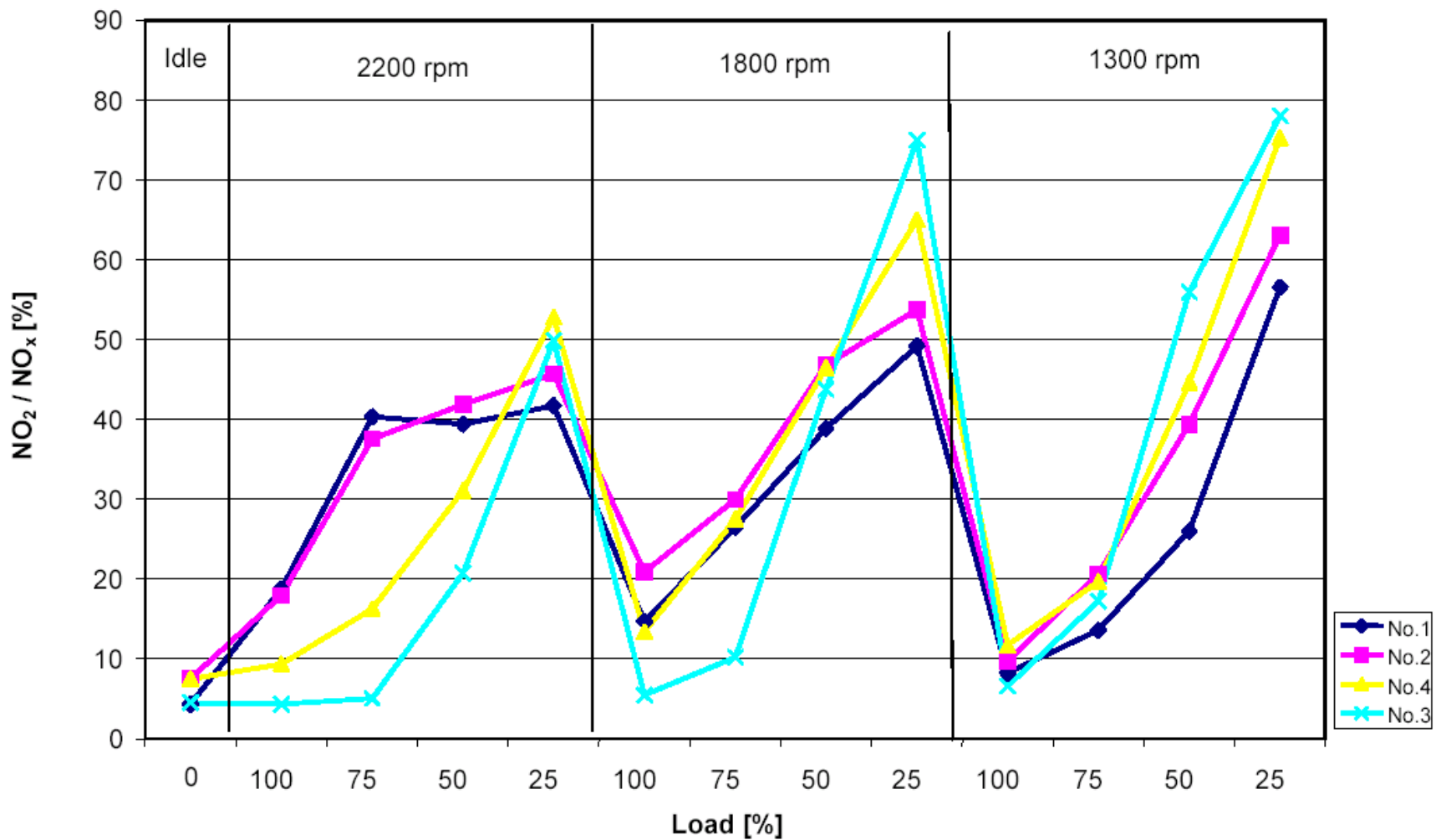




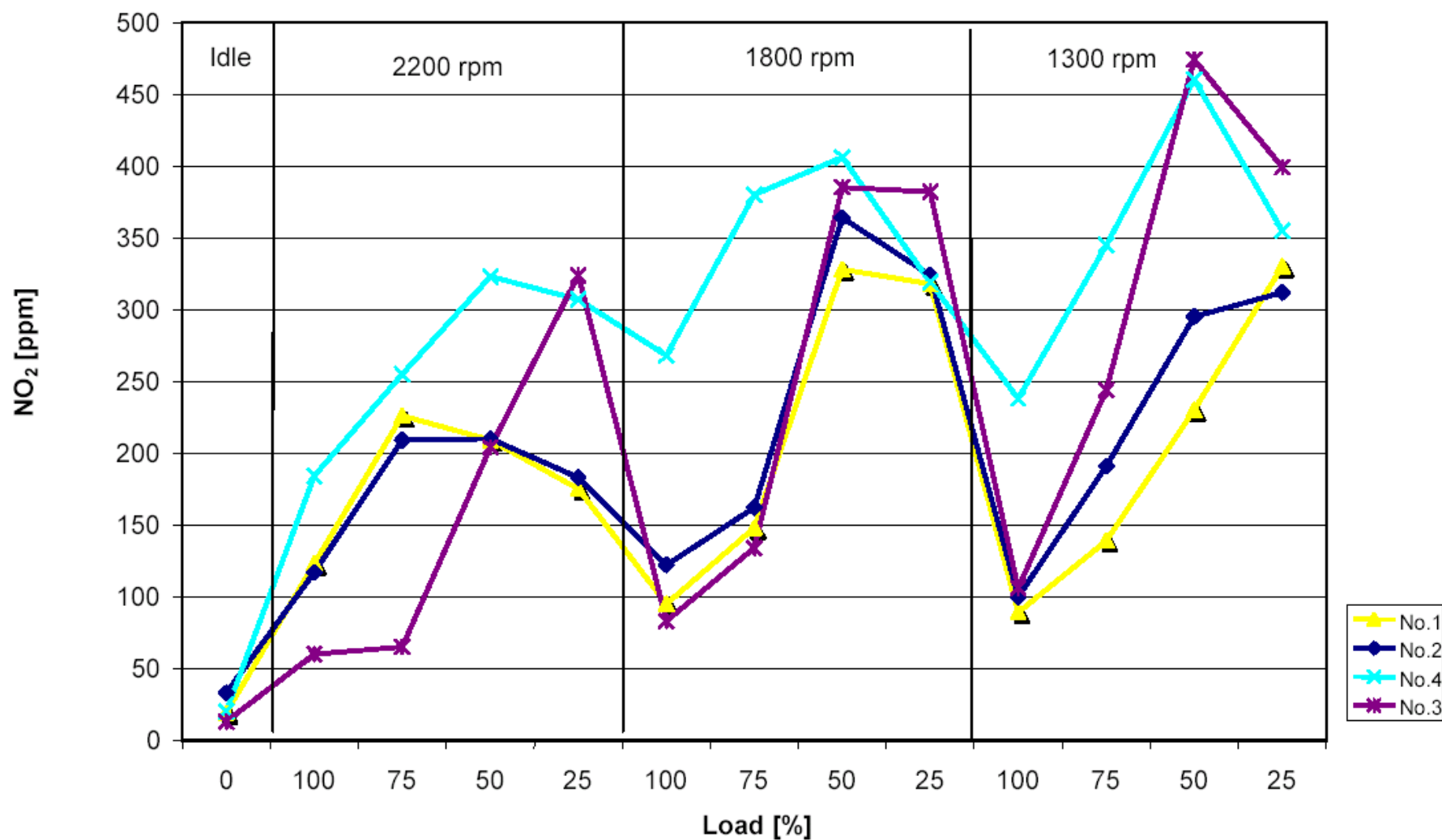
Fig. 4: Nitrogen oxide concentrations from vehicle No. 4 (SG 221820)



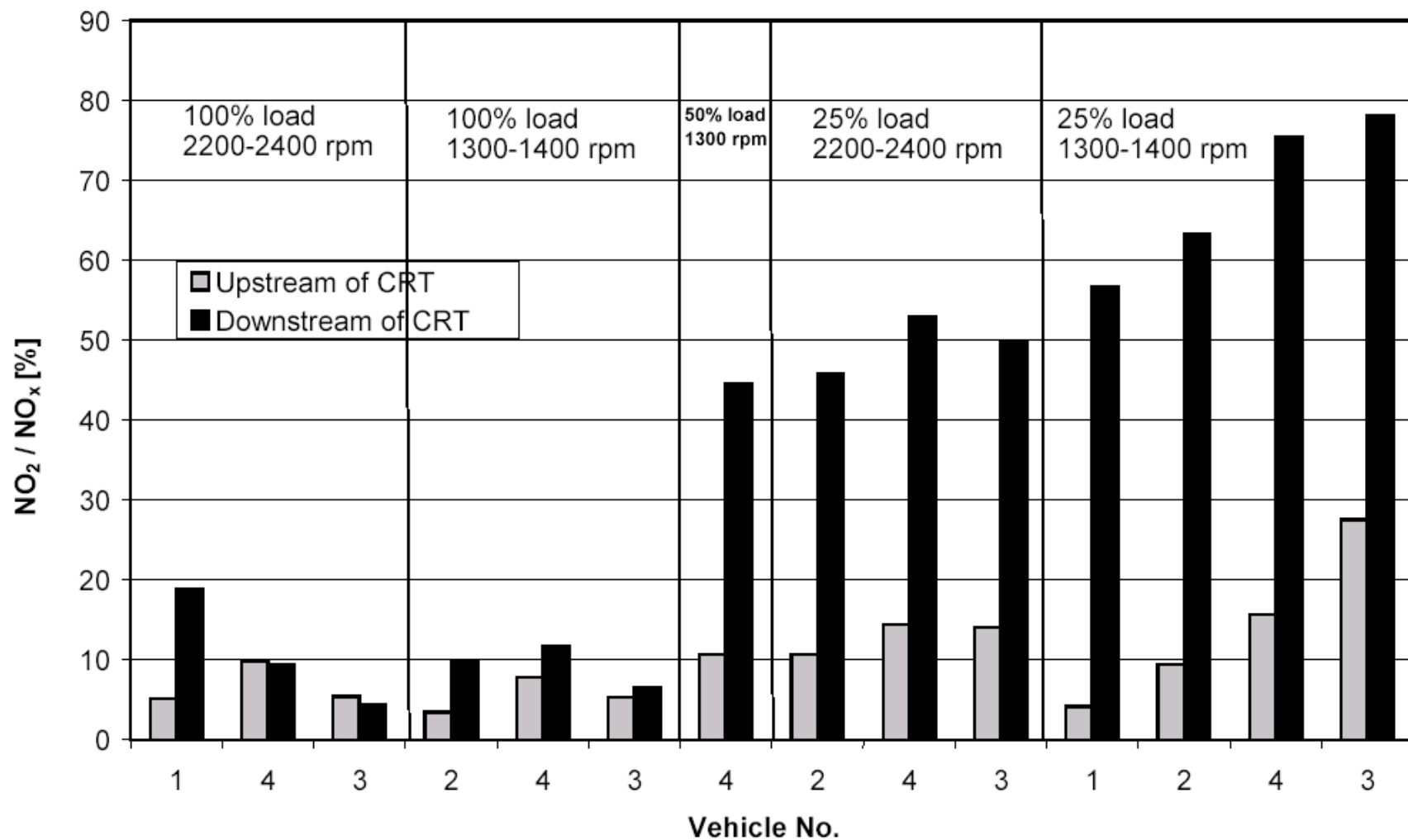
*Fig. 5: Nitrogen dioxide fraction vs. load*



*Fig. 6: Nitrogen dioxide concentration vs. load*



*Fig. 7: Nitrogen dioxide fraction upstream and downstream of CRT system*



*Fig. 8: Nitrogen dioxide concentrations upstream and downstream of CRT system*

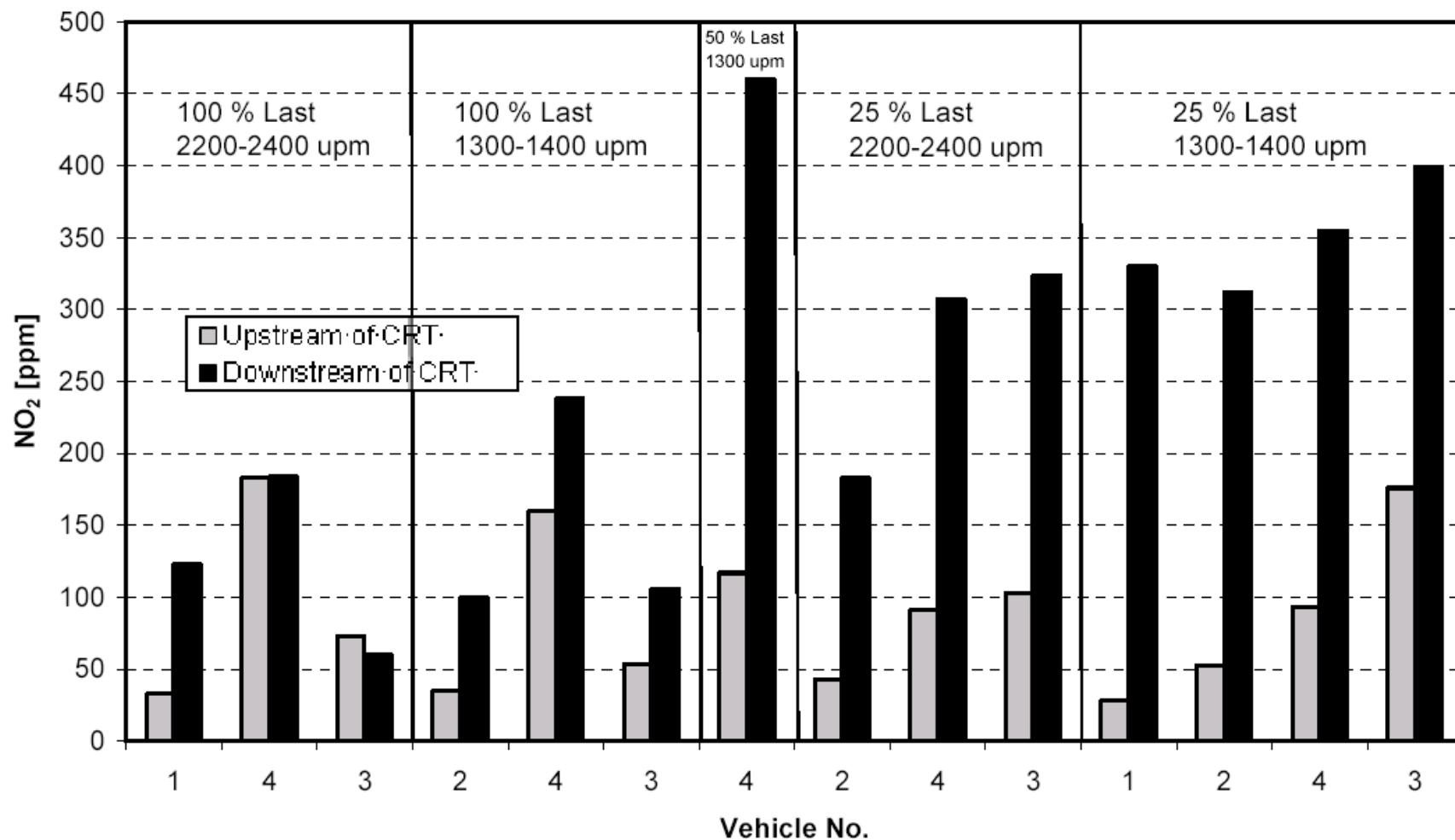
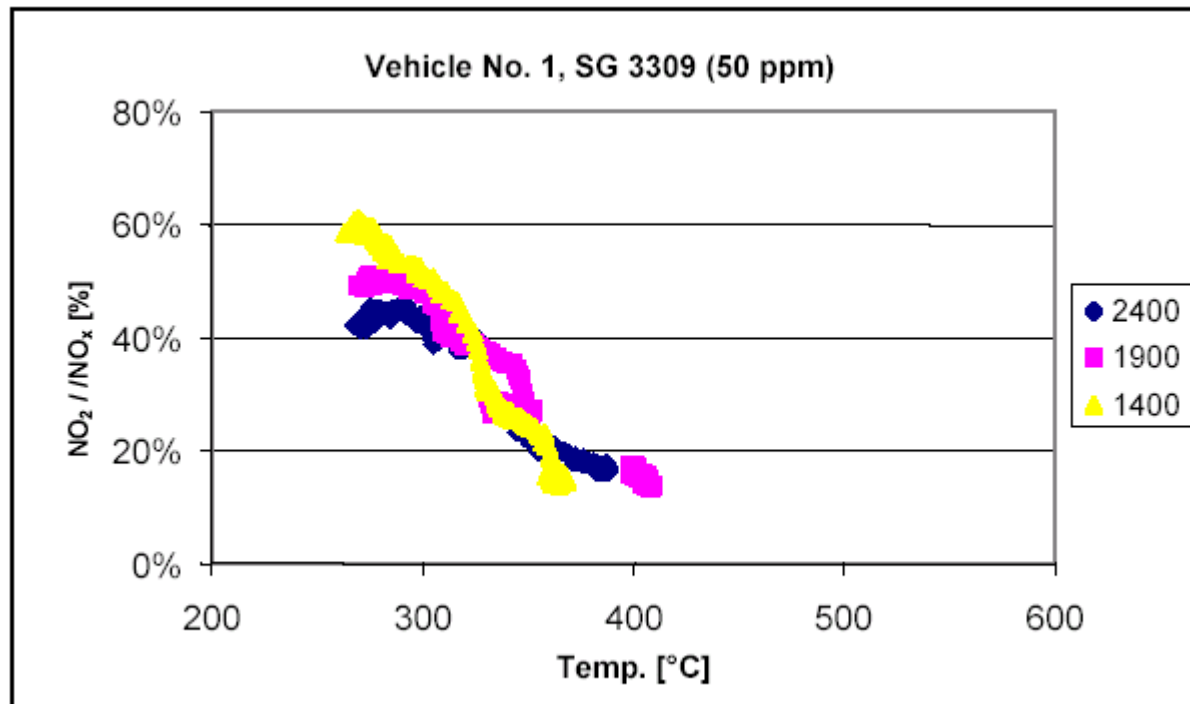
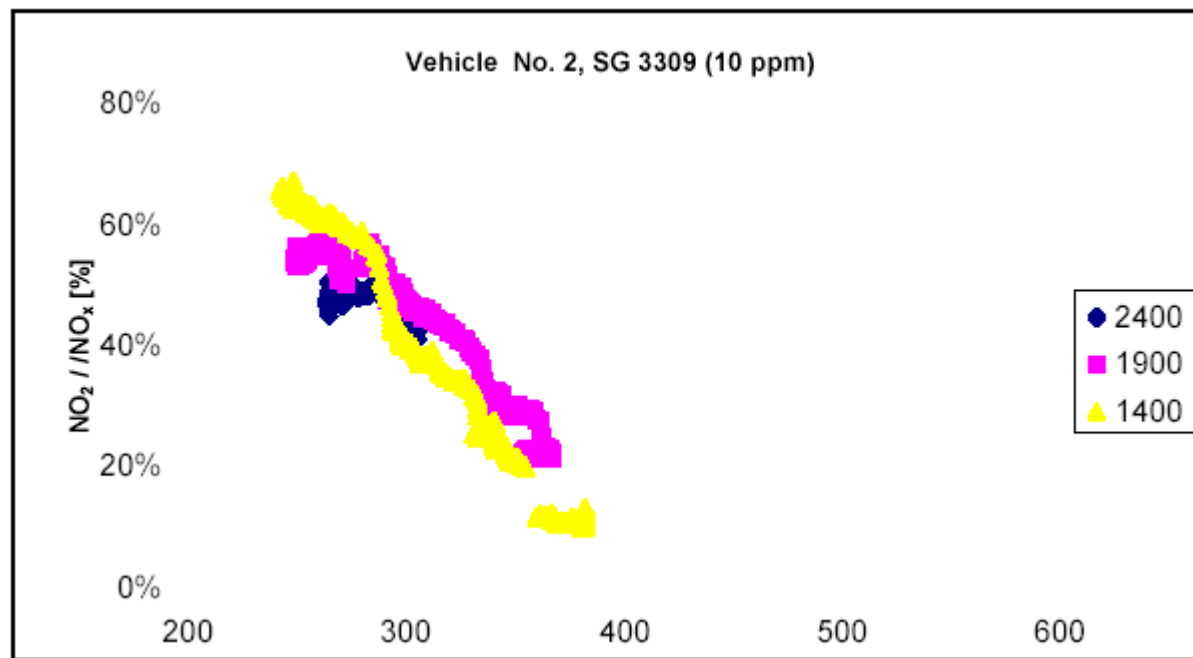
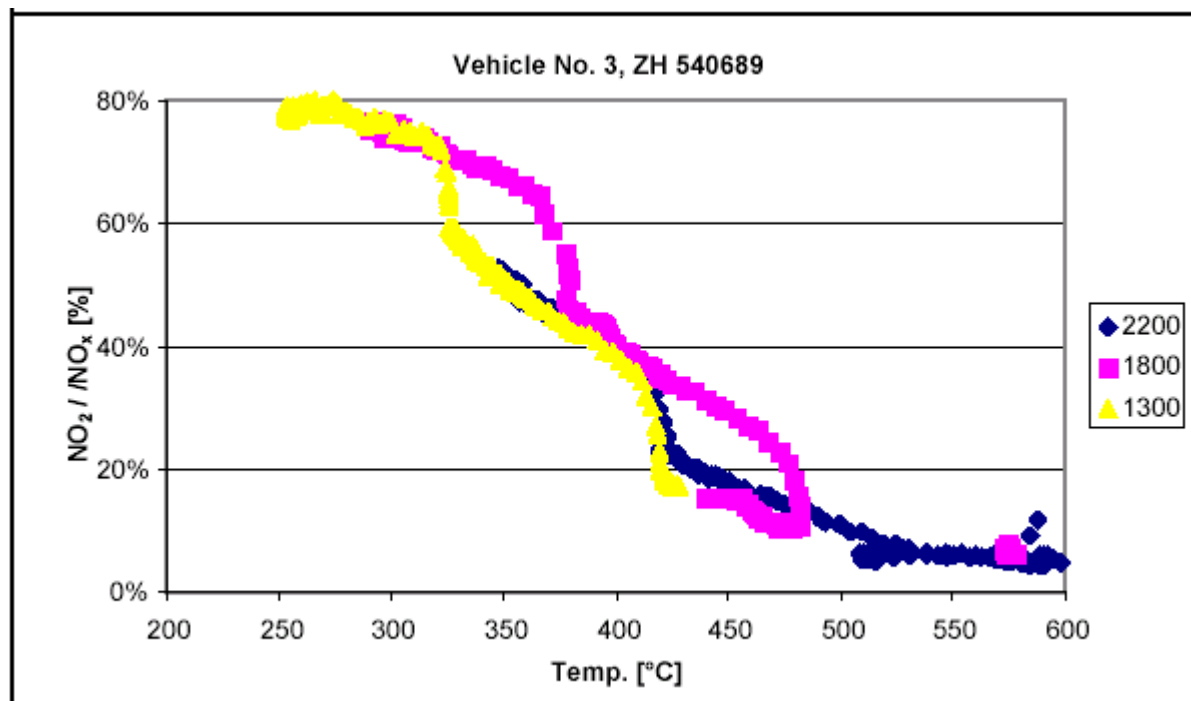


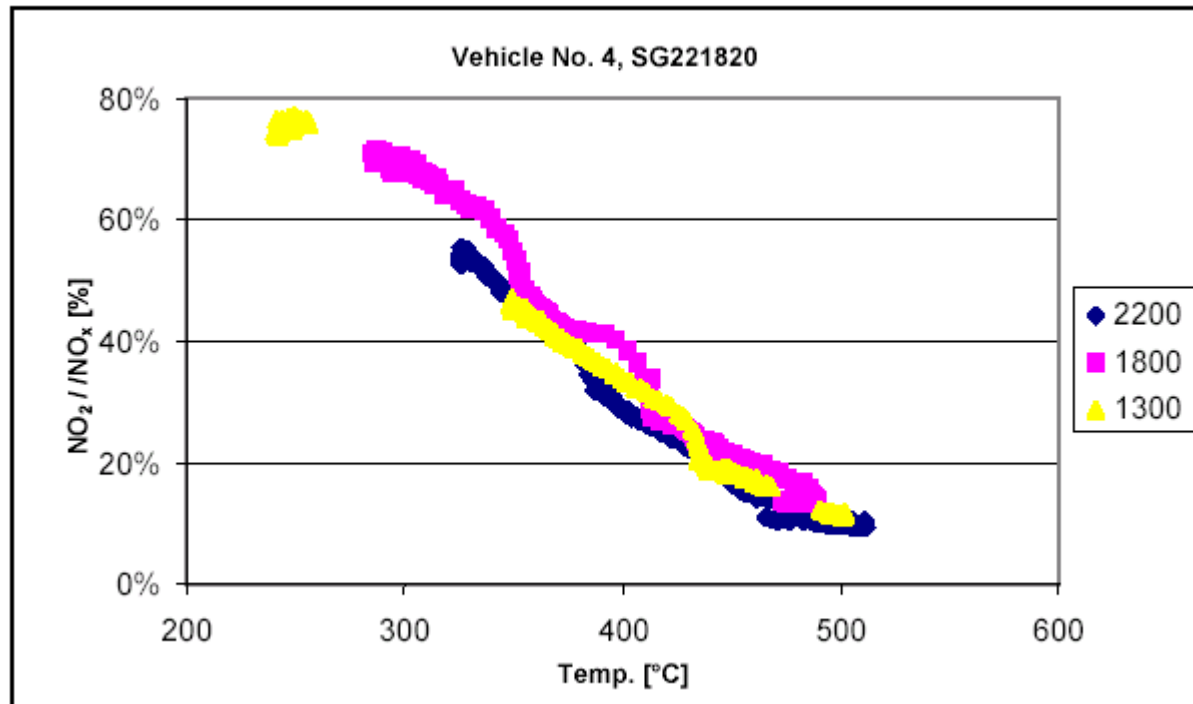
Fig. 9: Formation of nitrogen dioxide ( $\text{NO}_2/\text{NO}_x$ ) as a function of exhaust gas temperature and speed











# Mains results

- $\text{NO}_2$  / $\text{NO}_x$  ratio upstream of CRT are highly variable with engine type and operating conditions (5 to 30%)
- Downstream of CRT, at low load & low speed, the ratio can reach 80%, with a lowest at 55%
- Downstream of CRT, at low load & medium speed, the variation from an engine to another one is smaller, ratio are between 45 and 55%
- These areas of engine map are representative of city driving conditions and, in the USA, typical of operating conditions of school buses and urban vehicles.

# US perspectives

- No US engines were tested by EMPA, they could behave differently
- Recommendation is to check US engines not on the transient test cycle (mainly representative of highway driving) but on city driving cycles and better on some steady state points which are supposed to induce the highest ratio of NO<sub>2</sub>

# NO<sub>2</sub> levels are highly dependent of operating conditions

*courtesy of VERT*

## Type of Catalyzed DPF

### CRF #3

mean	mean	mean
NO <sub>2</sub> /NO <sub>x</sub>	Temp.	NO <sub>2</sub>
[%]	[°C]	[ppm]
14%	457	153
33%	405	290
57%	332	328
35%	208	68
17%	443	330
38%	399	600
64%	317	658
0%	121	0

### CRF #4

mean	mean	mean
NO <sub>2</sub> /NO <sub>x</sub>	Temp.	NO <sub>2</sub>
[%]	[°C]	[ppm]
14%	464	160
30%	406	265
56%	332	300
38%	210	78
16%	446	338
28%	397	425
49%	315	440
10%	119	25

## Without DPF

mean	mean	mean
NO <sub>2</sub> /NO <sub>x</sub>	T5	NO <sub>2</sub>
[%]	[°C]	[ppm]
2%	442	25
2%	392	15
4%	325	23
14%	206	28
1%	440	13
0%	396	5
2%	316	25
24%	118	48

mean	mean	mean
NO <sub>2</sub> /NO <sub>x</sub>	T5	NO <sub>2</sub>
[%]	[°C]	[ppm]
6%	447	75
6%	390	58
7%	326	48
19%	207	40
5%	442	118
6%	390	103
7%	312	80
25%	116	50

# NO<sub>2</sub> emissions with non PGM coated systems

*courtesy of VERT*

## DPF type

2000 rpm / full load  
2000 rpm / 375 Nm  
2000 rpm / 250 Nm  
2000 rpm / 50 Nm  
1400 rpm / full load  
1400 rpm / 440 Nm  
1400 rpm / 292 Nm  
Idle (790 rpm)

## Thermal regeneration

mean	mean	mean
NO <sub>2</sub> /NO <sub>x</sub>	Temp.	NO <sub>2</sub>
[%]	[°C]	[ppm]
1%	484	8
0%	417	5
1%	343	5
9%	215	23
1%	463	18
1%	423	10
0%	323	5
22%	103	43
mean	mean	mean
NO <sub>2</sub> /NO <sub>x</sub>	Temp.	NO <sub>2</sub>
[%]	[°C]	[ppm]
3%	445	40
4%	389	35
5%	323	35
20%	206	48
1%	445	30
2%	396	38
3%	315	35
33%	102	63

## Without DPF

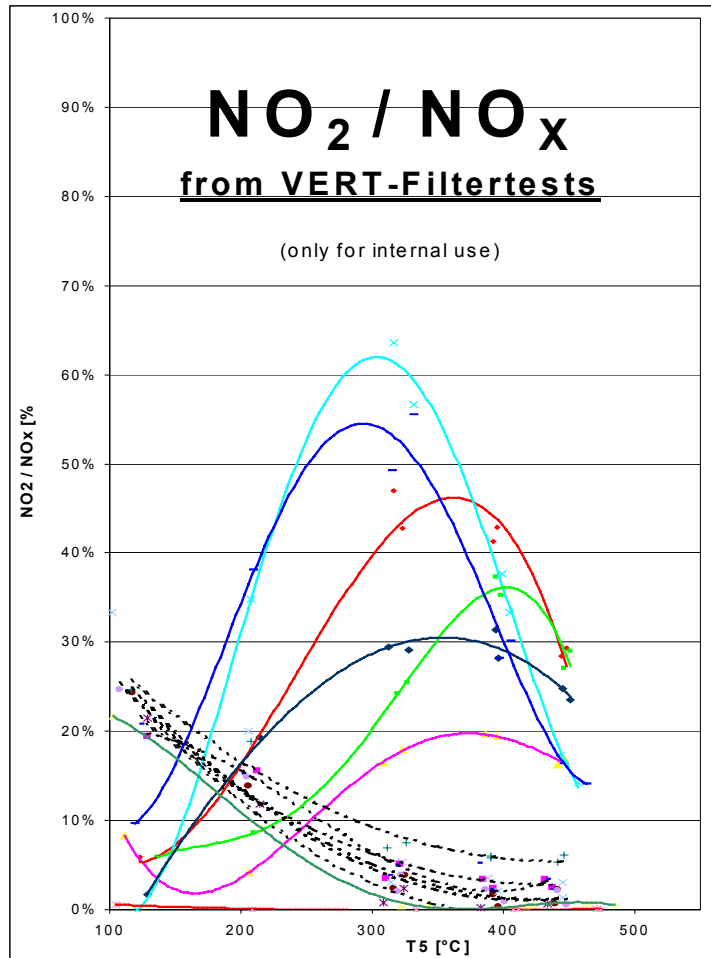
2000 rpm / full load  
2000 rpm / 375 Nm  
2000 rpm / 250 Nm  
2000 rpm / 50 Nm  
1400 rpm / full load  
1400 rpm / 440 Nm  
1400 rpm / 292 Nm  
Idle (790 rpm)

## Base metal cat DPF + FBC

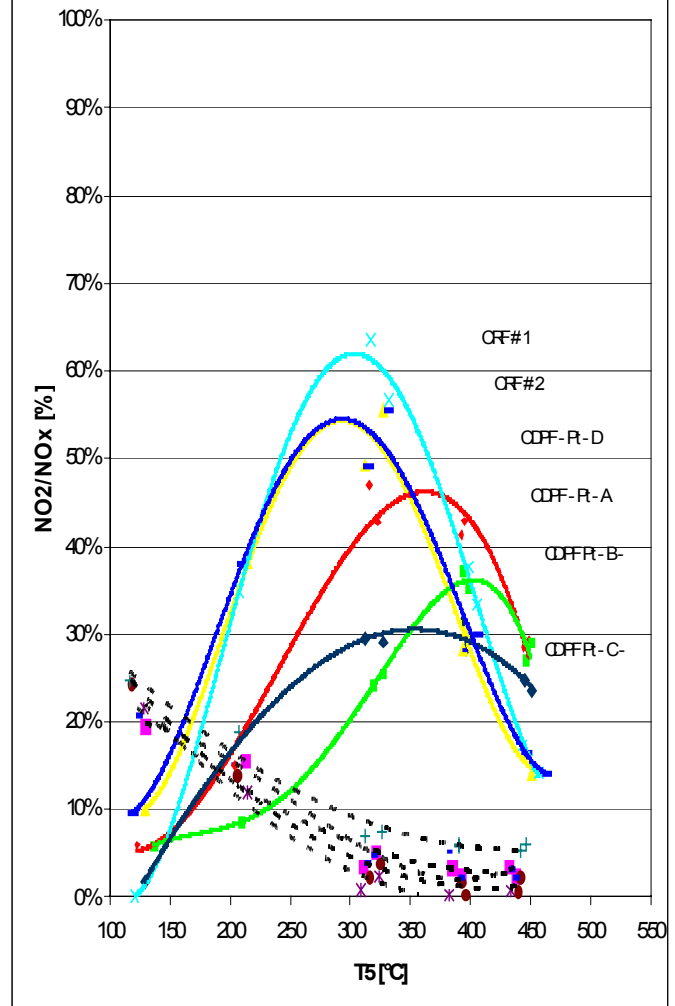
mean	mean	mean
NO <sub>2</sub> /NO <sub>x</sub>	Temp.	NO <sub>2</sub>
[%]	[°C]	[ppm]
0%	474	0
0%	408	0
0%	334	0
0%	209	0
0%	471	3
0%	411	3
0%	322	-3
1%	105	1
mean	mean	mean
NO <sub>2</sub> /NO <sub>x</sub>	Temp.	NO <sub>2</sub>
[%]	[°C]	[ppm]
2%	441	30
2%	387	25
4%	322	28
15%	205	35
1%	448	13
1%	401	18
2%	320	25
25%	107	50

# Overall results on different systems

Recently *courtesy of VERT*



One year ago



# NIOSH report April 1, 2004 on Stillwater mine experiment

## *During normal mining operations*

“Both tests #2 and # 3 were terminated, during the sampling period, due to high concentrations of NO<sub>2</sub> detected by the personal multi-gas monitor carried by the operator of the truck #921 35. During test #2, while vehicles #92 135 and #92535 were at the development section, **the monitor showed NO<sub>2</sub> concentrations higher than 5 ppm**, the 1973 ACGIH short term exposure level (STEL) for this gas adopted by MSHA (30 CFR 57.5001 1995). During test #3, when vehicle #92 135 was at the orepass, **the monitor carried by the operator showed concentrations in excess of 5 ppm. Elevated NO<sub>2</sub> exposures resulted in the removal of personnel from the work area.** Exposures above 5 ppm were not reported during test #4; however, the peak concentrations of NO<sub>2</sub> measured at the downstream sampling station (Figure 10) indicate that personal exposures might have been relatively high in this case as well.”

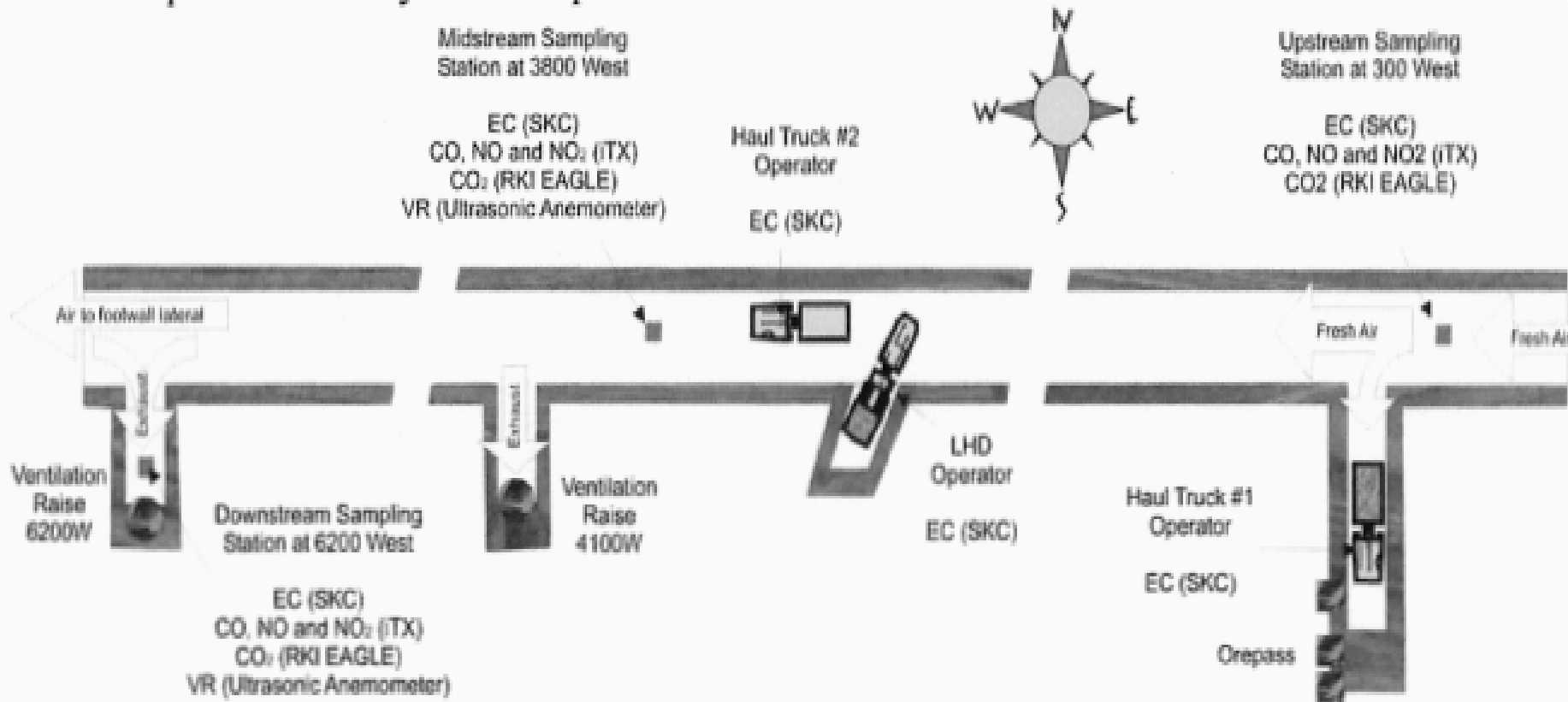
page 19

*courtesy of NIOSH*

# NIOSH Stillwater test site

## During normal mining operations

the development muck bay to the orepass.



**Figure 1. Schematic of the test zone (not to scale)**

*courtesy of NIOSH*



# Stillwater in remote gallery

courtesy of NIOSH

**Measured in a remote gallery, the tested vehicle being alone**

**Table 11. Normalized concentrations of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), nitric oxide (NO), and nitrogen dioxide (NO<sub>2</sub>) at downstream sampling station**

Test Type	CO [ppm]		CO <sub>2</sub> [ppm]		NO [ppm]		NO <sub>2</sub> [ppm]	
	Max.	Ave.	Max.	Ave.	Max.	Ave.	Max.	Ave.
<b>#92128 Haul Truck, MSHA vent rate 12000 cfm</b>								
Baseline	11.1	6.7	3834	2924	22.2	16.9	1.1	0.6
Engelhard DPX	0.0	0.0	3793	2718	18.9	12.5	3.2	2.1
<b>#92506 LHD, MSHA vent rate 11500 cfm</b>								
Baseline, D1	18.5	2.3	6268	2104	27.7	5.0	0.9	0.0
Baseline, D2	18.4	2.6	5874	2201	23.0	5.3	0.9	0.0
<b>#92526 LHD, MSHA vent rate 10000 cfm</b>								
Baseline	17.5	6.4	7820	3699	40.8	17.0	2.6	0.9
Baseline / PTX	0.0	0.0	7622	3821	41.3	18.6	2.9	1.0
Biodiesel B20 / PTX	0.0	0.0	7450	3826	40.1	19.3	2.9	1.1
Biodiesel B50 / PTX	0.0	0.0	7622	3855	44.2	21.1	3.5	1.3
<b>#99942 LHD, MSHA vent rate 15000 cfm</b>								
Baseline, D1	24.2	4.5	8740	2849	50.2	13.5	3.1	0.6
Baseline, D2	23.4	4.4	9028	2861	43.3	11.2	2.7	0.5
DCL MineX	0.0	0.0	8656	2713	43.3	11.2	5.7	1.5

# Stillwater NO<sub>2</sub> in remote gallery

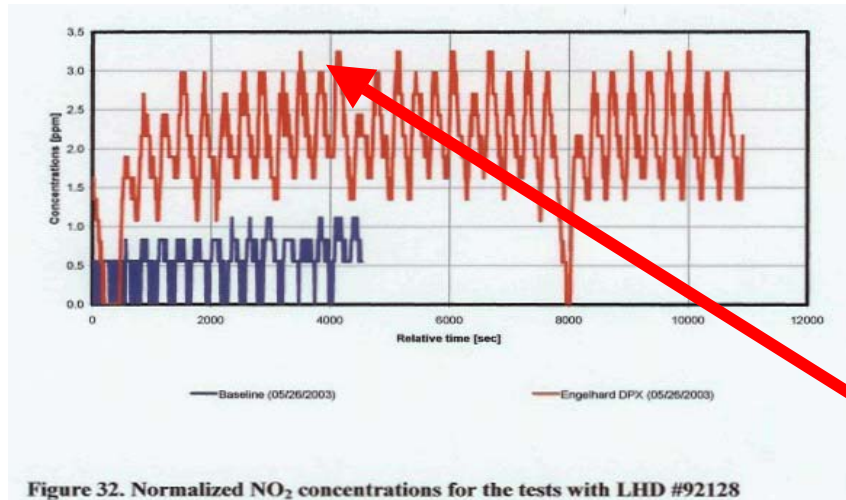


Figure 32. Normalized NO<sub>2</sub> concentrations for the tests with LHD #92128

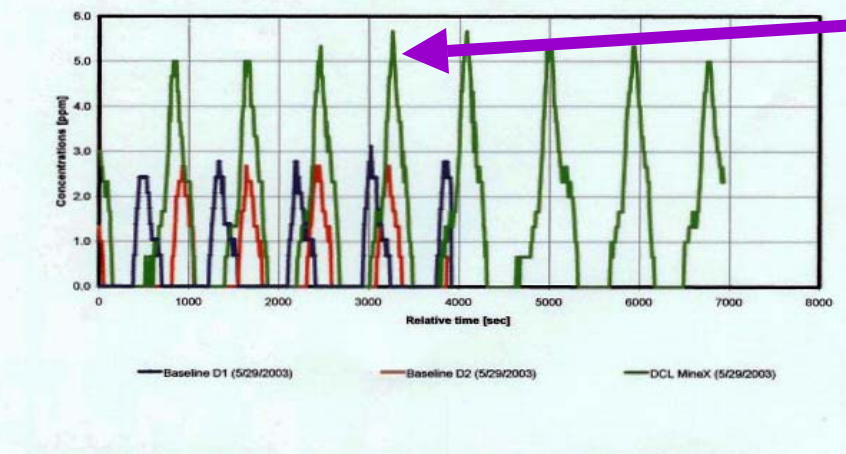


Figure 33. Normalized NO<sub>2</sub> concentrations for the tests with LHD #99942

- With only one vehicle equipped with commercial CDPF in a remote gallery, the limit of 3 ppm, which is the legal exposure during 15 mn, is regularly met or even exceeded
- Engine base lines varie but for the people exposed to the emission the only valid limit is the threshold of exposure

courtesy of NIOSH

# Original report available at EMPA

**Report on FBC (Octel) + base metal catalyzed SiC filter (Haldor Topsoe)**

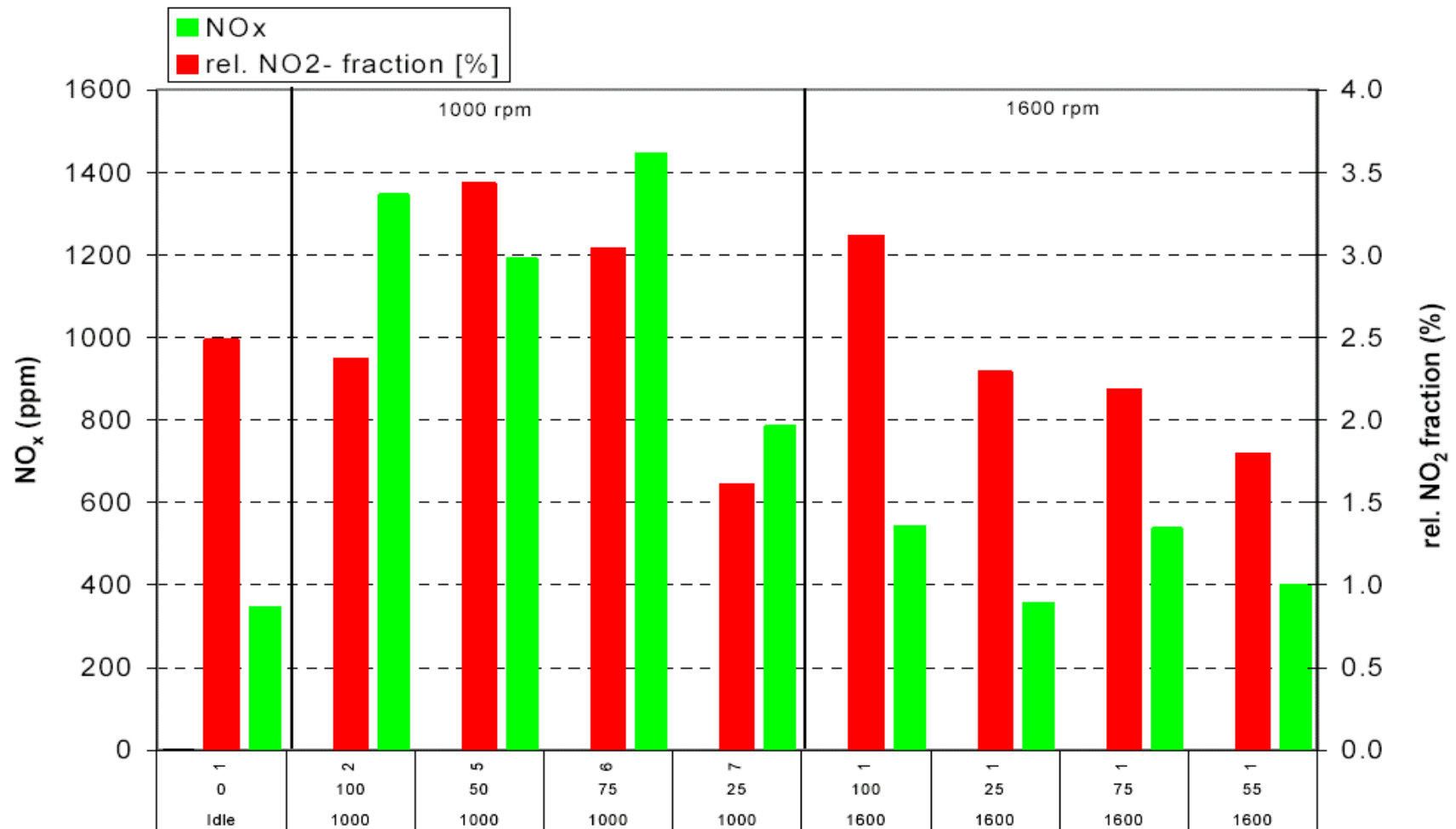
Report No. 433'356  
Air Pollution / Environmental Technology Laboratory



**Contact at EMPA: Lukas Emmenegger** [lukas.emmenegger@empa.ch](mailto:lukas.emmenegger@empa.ch)

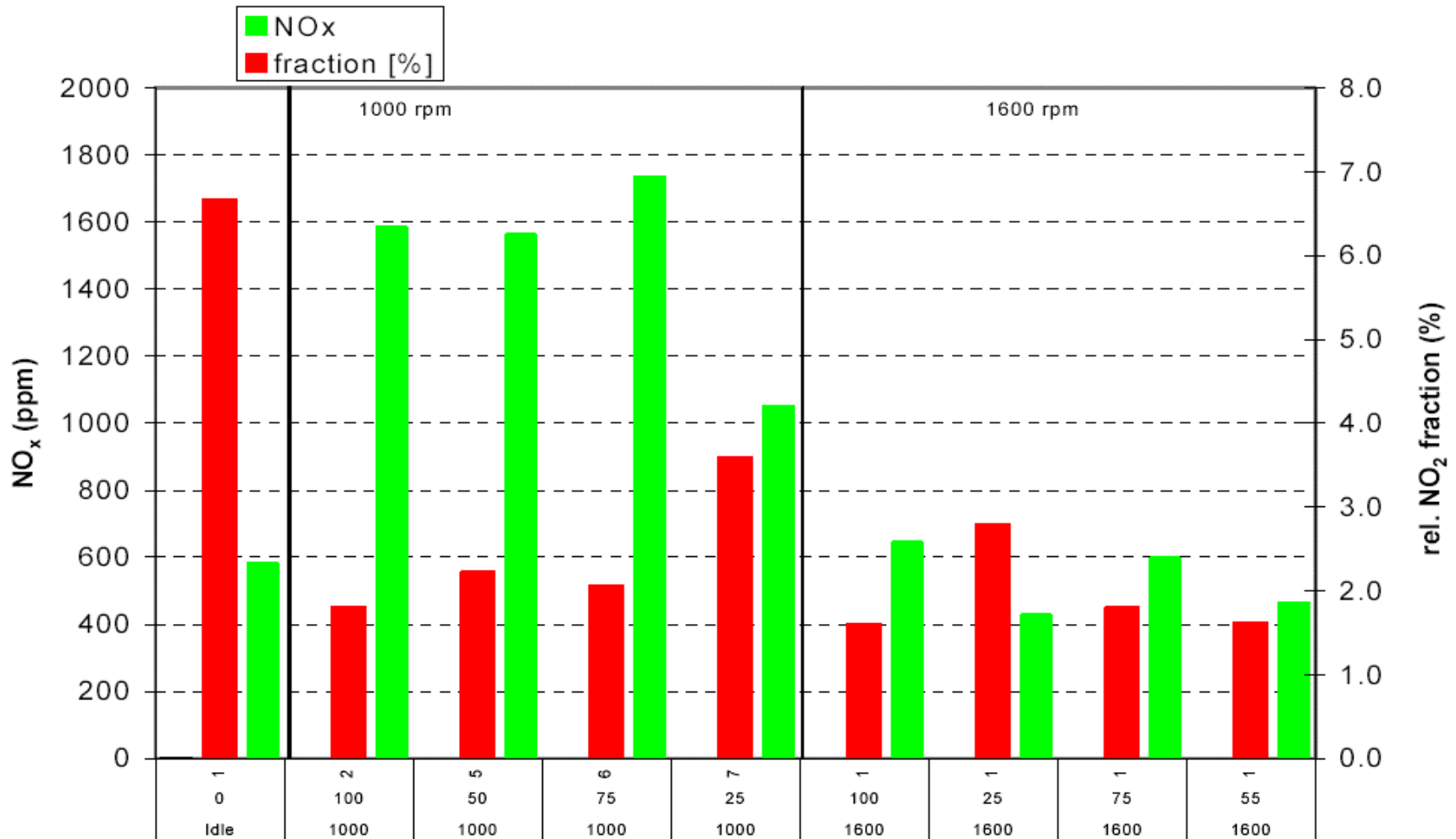
# Alternative system with FBC

Figure 1: Ratio of nitrogen oxide concentrations downstream of filter



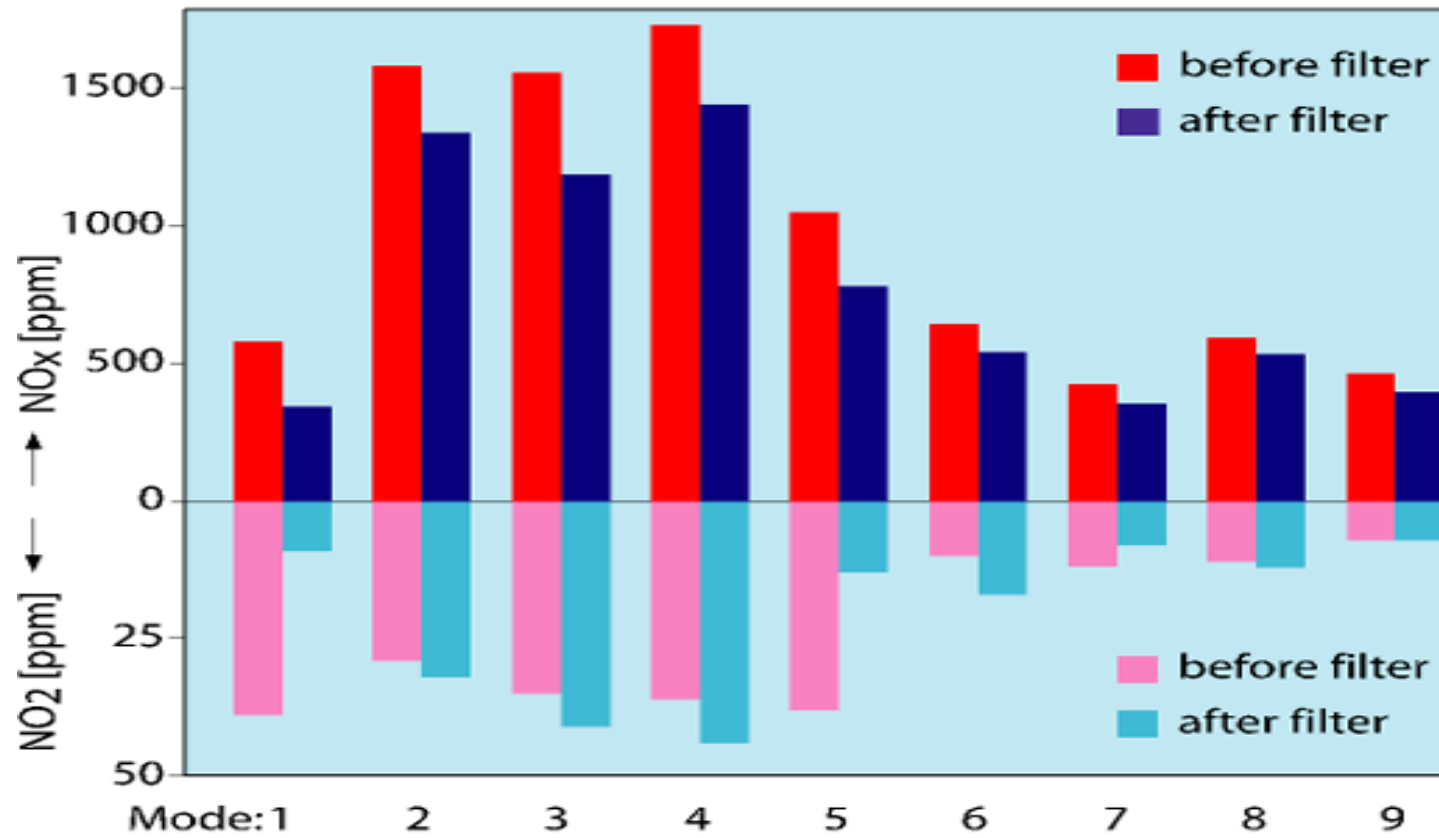
# Alternative system with FBC

Figure 2: Ratio of nitrogen oxide concentrations upstream of filter



# Alternative system with FBC on a Euro 3 bus

NO<sub>x</sub>- and NO<sub>2</sub>-emissions with VERT particle filter  
base metal coated + FBC

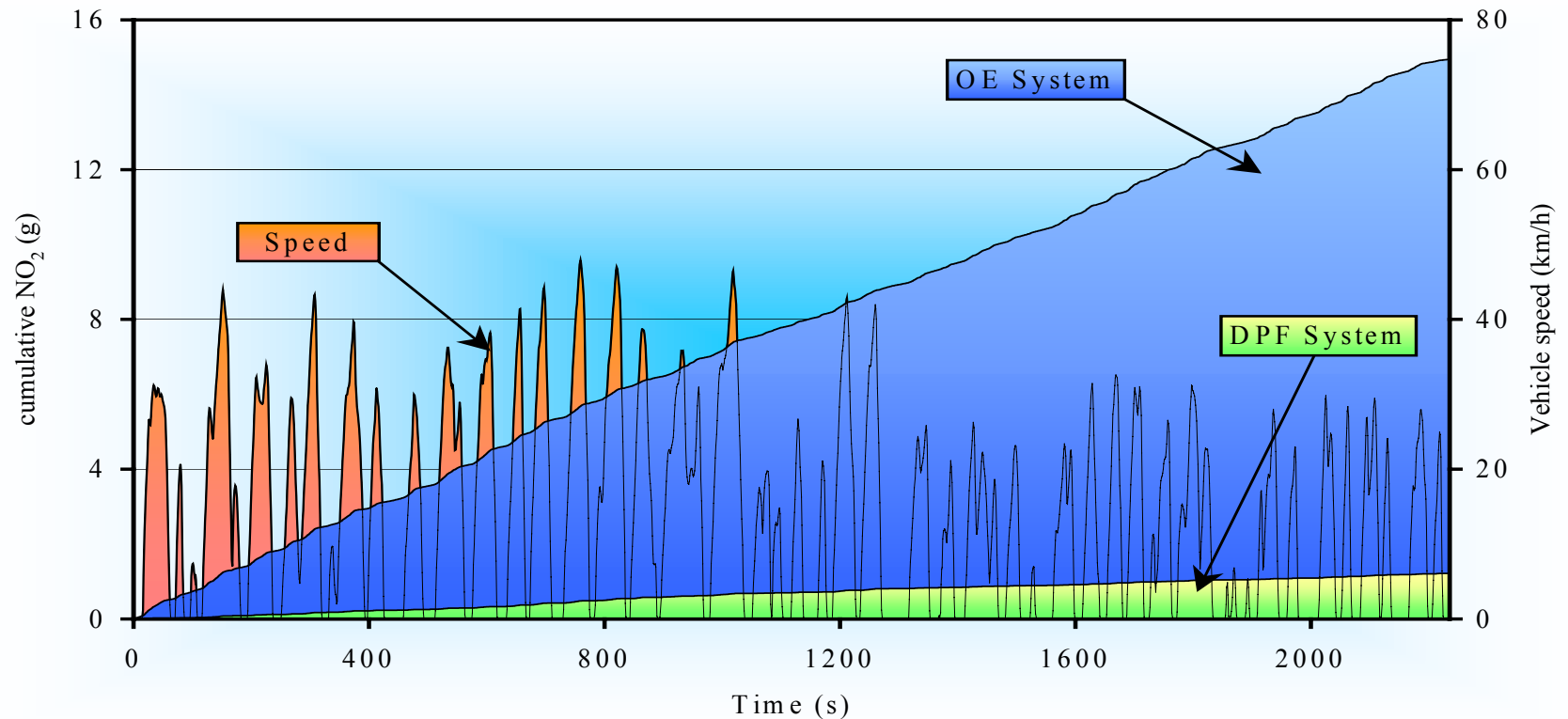


Vehicle: Volvo B12BLL, Euro 3  
Test: ESC 9 mode stationary

# Further field application of DPF + FBC

## Cumulative NO<sub>2</sub> emissions

courtesy of ADASRA-OCTEL



# Hot or cold measurements of NO<sub>x</sub> and NO<sub>2</sub>

- Temperature of gases is a key factor of accuracy when measuring NO<sub>x</sub> and NO<sub>2</sub>
- NO<sub>2</sub> value is in fact NO<sub>x</sub> – NO
- Following graphs are extracted from a Swiss study (Biel University) and show the huge influence of temperatures
- Another conclusion is that FBC does not produce NO<sub>2</sub>, while CRT produces a lot especially detectable in hot gas flow



# Hot and cold measurements

## Discussion

- It is hardly believable that only a change of temperature can justify this difference in  $\text{NO}_2$  levels: we believe that explanation is more likely in the fast reactivity of  $\text{NO}_2$  with water to give  $\text{HNO}_3$  which is no more measured as  $\text{NO}_x$
- If there is some condensed water in cold measurement circuit, the level of  $\text{NO}_x$  which is measured is reduced and therefore the level of  $\text{NO}_2$

# NO<sub>x</sub> & NO<sub>2</sub> with CRT

*courtesy of Bielefeld University*

Vergleich der NO<sub>2</sub> - Werte bei kalter und heisser Messung  
mit CRT Partikelfilter & Dieselkraftstoff < 50 ppm; Liebherr D914T

NO<sub>2</sub> = NO<sub>x</sub> - NO

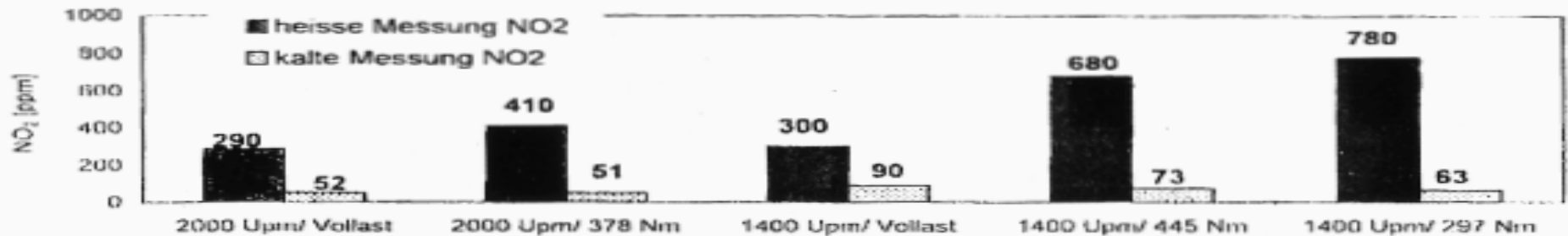


Figure 3

Vergleich der NO<sub>x</sub> - Werte bei kalter und heisser Messung  
mit CRT Partikelfilter & Dieselkraftstoff < 50 ppm; Liebherr D914T

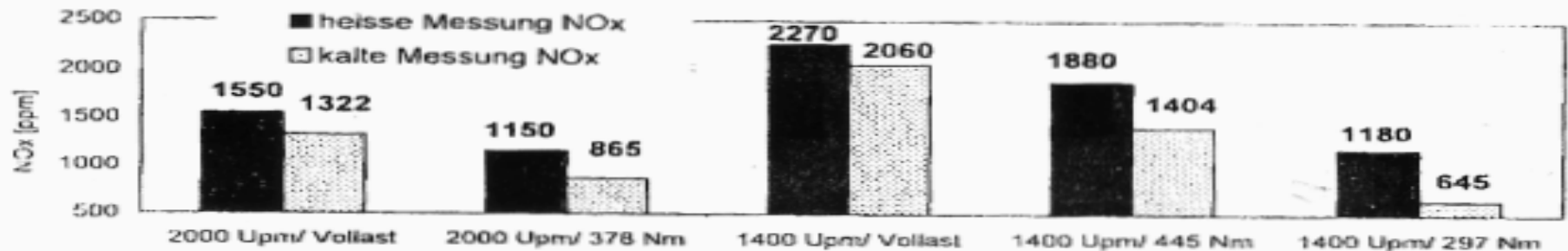


Figure 4

# NO<sub>x</sub> & NO<sub>2</sub> produced by FBC

courtesy of Biel University

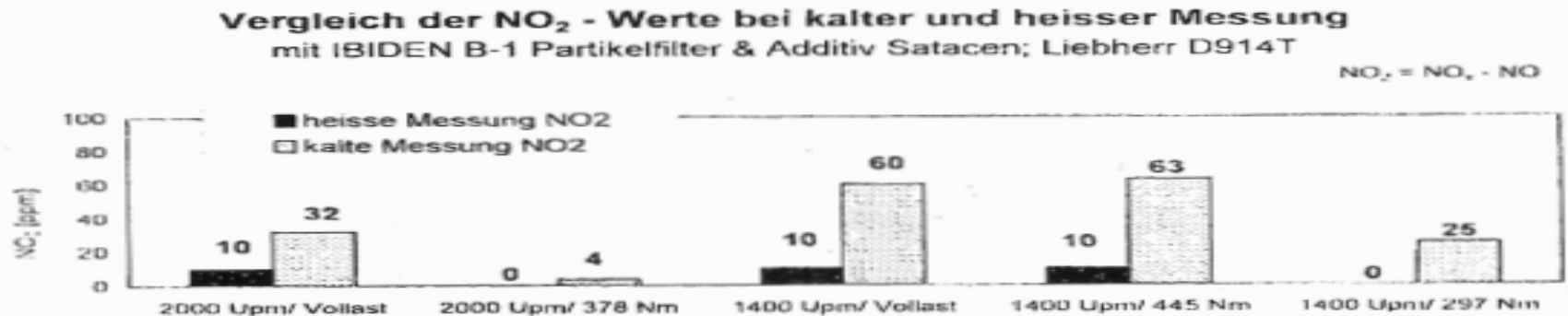


Figure 1

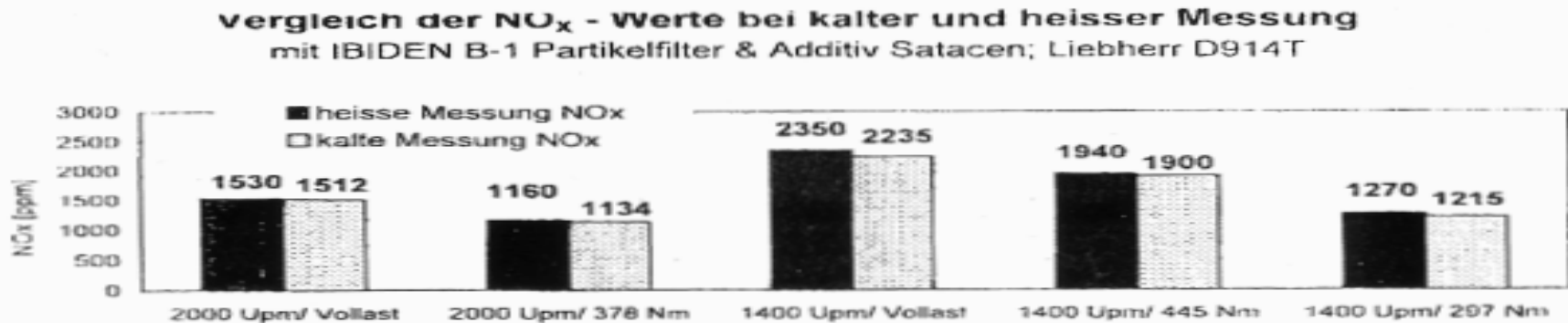


Figure 2

# Discussion ( 1 )

- No discussion about the necessity to eliminate the PM by using appropriate filters
- The discussion about counting or not the liquid droplets represent a risk to delay any decision while most of the specialists in health effects admit today that the droplets have a risk factor which must be related with their mass, while solid soot risk must be related with size and number

# Discussion ( 2 )

For BUWAL appropriate means:

- filters efficiencies must be also measured by number in order to eliminate problems linked with mass measurements (but mass measurement must be kept for reference)
- ability to avoid formation of NO<sub>2</sub> in all operating conditions must be a bonus in the process of verification of exhaust controls
- not to exceed limits have to be defined on city driving cycles or on steady state tests

# Conclusions ( 1 )

- Filter efficiency must be qualified by ability to remove all categories of soot particles from the exhaust stream (only number give an accurate rating)
- Exposure risks due to high levels of NO<sub>2</sub> emissions downstream of DOCs and filter systems containing Platinum must be taken in account in any verification procedure

# Conclusion ( 2 )

- Measuring NO<sub>2</sub> on transient cycles does not reflect the risk of exposure in micro-environnements (cabin of vehicles or buses, spot places where school buses or urban vehicles agglomerate, road tunnels)
- Only measurements on selected steady states (for the same reason EST was introduced in certification (NO<sub>x</sub>) of HD engines) together with NTE limits will give an accurate evaluation of risks

# Discussion ( 3 )

- Another approach could be to measure  $\text{NO}_2$  on city driving cycles, as developed in certain cities. These cycles include a majority of low speed / low load engine operating conditions where the formation of  $\text{NO}_2$  is maximum
- It could be premature to define any type of regulation before achieving individual exposure risk evaluation in field conditions



# Acknowledgements

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ADASTRA – OCTEL: Paul Richards